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(54) Liquid crystalline material and display cell containing said material.

(57) A liquid crystalline material in the form of an anisotropic gel comprising a polymerized liquid crystalline material and a low-molecular liquid crystalline material, can be used in a display cell, said polymerized material forming a permanently oriented network in the low-molecular liquid crystalline material. The display cell comprises two opposite plates 1 and 2 which are transparent to light as the substrate, which plates are provided with electrodes 4 and 5 of a material which is transparent to light on the sides facing each other, orientation layers 7 being provided on said electrodes. A sealing material 3 is provided between the ends of the plates 1 and 2. The space between the plates and the sealing material is filled with the liquid crystalline material 6.

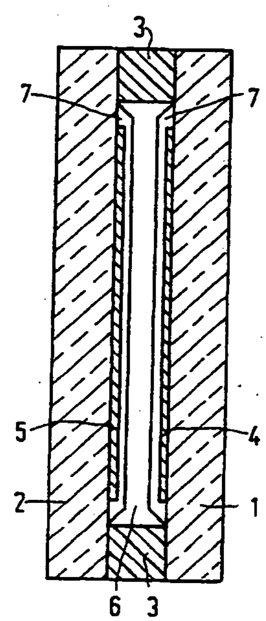

FIG.1

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The invention relates to a liquid crystalline material in the form of an anisotropic gel comprising a polymerized liquid crystalline material and a low-molecular liquid crystalline material. The invention further relates to a display cell comprising two opposite plates which are transparent to light as the substrate, which plates are provided with an electrode of a material which is transparent to light on the sides facing each other, said electrode carrying an orientation layer and a sealing material being provided between the ends of the plates, a liquid-crystalline material being introduced in the space between the plates and the sealing material which is in the form of, for example, a ring.

In WO 89/09807, a material is disclosed which consists of microdrops of a liquid crystalline material dispersed in a polymeric matrix of a material having mesogenic groups, i.e. a liquid crystalline material. In said publication it is stated that the matrix material is of the thermoplastic type and, hence, as the substances constituting the matrix material linear polymers are indicated. Said linear polymers can be used in electro-optical light shutters because, dependent upon the structure of the microdrops and the configuration of the light shutter, said light shutters are translucent in the OFF-state and opaque in the ON state, or conversely.

In WO 89/06371, a composite material is disclosed which consists of drops of liquid crystalline material within a matrix of a polymer of acrylic acid, said liquid crystalline material having a solubility in the polymer which is lower than the solubility in the corresponding monomer. After polymerization of the monomer, this composite material is a solid matrix in which the liquid crystalline material is dispersed in the form of drops. In this manner, problems concerning the leaking of the liquid material from the display cells are overcome. In WO 89/06264, a similar material is disclosed, with this difference that a matrix is formed from a copolymer of an acrylate and a mercaptan.

In European Patent Application EP 291427, a description is given of a polymer of a liquid crystalline material having mesogenic groups in the side chain and an ethene-like unsaturation. These linear polymers may be mixed with variable quantities of small molecules which have no side chains, which small molecules may be mesogenic. The orientation of the linear polymers can be changed when the external field is changed, whereas the orientation of a network remains unchanged.

European Patent Application EP 313053 describes the use of a liquid crystalline material having a positive dielectric anisotropy and a transparent solid which is present in the liquid crystalline material in the form of particles on a three-dimensional network. Said network, however, is not composed of a liquid crystalline material and it is not oriented.

In an article by Rudolf Zentel, published in Liquid Crystals, 1986, Vol. 1, No. 6, pages 589-592, it is described that cross-linked crystalline polymers are made to swell by using low-molecular nematic liquid crystal materials, so that orientation in electric fields can be brought about more readily. In fact, two polymer materials are used, such as 1) polyacrylate having side groups to obtain a liquid crystalline material and 2) polymethacrylate. Both polymer materials have a different cross-linking density.

In accordance with the invention, a liquid crystalline material as described in the opening paragraph is obtained, which is characterized in that the polymerized material a) forms a permanently oriented network in the low-molecular liquid crystalline material b). Preferably, said material b) forms a continuous phase around the network of material a). This preferred continuous phase is obtained, in particular, by selecting the quantity by weight of material a) to be smaller than 50 % of the sum of material a) and material b), namely between 1 and 25 % by weight and more specifically between 3 and 10 % by weight.

Examples of the liquid crystalline material a) from which a network can be formed are acrylates, epoxy compounds, vinyl ethers and thiolene systems. Examples of acrylates are represented by formula 1 and 2 of the formula sheet; in formula 1, A denotes a bonding dash or -O- or -COO-, m and n denote an integer between 0 and 20, and B denotes a mesogenic group as represented by formulae 9-12 on the formula sheet, or other examples of mesogenic groups such as -N=N-, and the like, which are known to those skilled in the art. Formula 2 represents an acrylate having a mesogenic group included in the chain, said mesogenic group being represented by formula 12 on the formula sheet.

An example of an epoxy compound is shown in formula 3, where X denotes a group having formulae 4-8, as shown on the formula sheet. In formulae 4-8, p denotes an integer having a value of 0-20 In formula 3, B has the same meaning as in formula 1.

An example of a vinyl ether, which may be used as a starting material for the material a) according to the invention, is represented by formula 13 on the formula sheet, the meaning of X and B being the same as described above with respect to formula 3.

Formulae 15-18 represent substances which can be used as material b), i.e. a substance which cannot be polymerized. A mixture of the compounds of formulae 15-18 is commercially available under the indication E7 by BDH, in quantities of 8 %, 25 %, and 16 %, respectively. It is alternatively

possible to use a liquid crystalline material as the material b), said liquid crystalline material having polymerizable groups which do not or hardly polymerise under the conditions of polymerisation for the formation of the network consisting of substance a).

Optical and electrical properties of a scatter-type liquid-crystal cell comprising the known anisotropic gel will be described in more detail with reference to the accompanying drawing, in which

Fig. 1 is a cross-sectional view of a display cell according to the invention;

Fig. 2 shows the normalized transmitted light intensity as a function of the effective voltage applied to the cell for gels having different compositions;

Fig. 3 shows the normalized scattered light intensity as a function of the angle between the plane of polarisation of the light incident on the cell and the direction of molecular orientation;

Fig. 4 shows the response of the cell comprising a gel having a specific composition for various applied voltages.

In Fig. 1, reference numerals 1 and 2 denote two opposite plates which are transparent to light and which will hereinafter be termed substrates and which comprise electrodes 4 and 5 on the opposing sides, said electrodes being manufactured from, for example, $In_2O_3.SnO_2$. On the electrode there is provided an orientation layer 7 of, for example, a polyamide or silane, by means of which the liquid crystalline material 6 according to the invention can be oriented between the electrodes. The cell is manufactured by arranging the substrates thus formed and provided with electrodes and the orientation layer opposite each other and closing the apertures by, for example, a ring-shaped member and filling the space between the substrates and the ring 3 with the liquid crystalline material 6 according to the invention. In practice, a bonding layer of an epoxy compound can be used instead of the ring 3 shown.

When no voltage is applied to the cell, light incident on said cell is scattered to a small degree only. By applying a voltage, the gel present in the cell is subjected to an electric field and the gel and, consequently, the cell become opaque as a result of the scattering produced. However, it is alternatively possible to use molecules having a negative dielectric anisotropy instead of molecules having a positive dielectric anisotropy, as a result of which the switching process is reversed. When a uniaxial orientation is used, the scattered light is highly polarized and is brought about only by the presence of the network. When a voltage is applied to the cell, only a part of the free molecules is reoriented. As a result of the high degree of "anchoring", free molecules which are close to the network molecules are less influenced by the electric field generated by applying the voltage.

As stated above, the cell is transparent when no voltage is applied and becomes more opaque according as the voltage applied increases. Fig. 2 shows the normalized transmitted light intensity I_T/I_O as a function of an effective voltage V_{rms} applied to a cell of 6 μm for gels containing different quantities of E7 and hence different quantities of C6H, the latter being 3 %, 5 %, 7 % and 10 %, respectively. At a low content of network molecules, the cell starts to scatter at approximately 16 volts. When the applied voltages are higher, scattering rapidly reaches a saturation level after which it decreases. The threshold voltage for bringing about scattering, however, increases rapidly according as the content of network molecules increases, whereas the slope at which the saturation level is reached becomes less steep. As stated above, the higher voltages necessary to attain reorientation of the free molecules is caused by the high degree of "anchoring" which is exerted by the network molecules on the neighbouring free molecules.

The effect of the direction of polarization on the intensity of the light passed is shown in Fig. 3 which depicts the scattered light intensity as a function of the angle θ between the plane of polarisation of the light incident on the cell and the direction of molecular orientation. As shown in Fig. 3, the maximum scattering is obtained when $\theta = 0°$, and hardly any scattering occurs when $\theta = 90°$. This means that the component of the light polarized in the direction perpendicular to the molecular orientation is passed almost without scattering. Starting from a uniaxial orientation of the gel molecules, the application of a voltage makes free molecules which are not strongly bonded to the network molecules reoriented themselves in accordance with the electric field generated. The long axes of the reoriented free molecules will be inclined relative to the initial direction of molecular orientation. In the case of uniaxial orientation scattering is maximally 50 %. To attain a higher percentage of scattering, non-uniaxial orientation, such as twisted or helicoidal orientation has to be used, while applying monomers having a chiral atom or using chiral doping. Thus, the twisted orientation can more readily be attained by using the gel in accordance with the invention.

Fig. 4 shows the effect of the applied voltage on the rise time and decay time. Fig. 4 relates to a cell of 6 μm having a gel containing 95 % of E7. Fig. 4 shows that the rise time decreases according as the applied voltage increases, whereas the decay times remain substantially constant up to the saturation voltage and tend to increase somewhat when the voltage is increased further. Besides, the

rise time increases according as the cell thickness increases, but the decay time remains constant. The decay time decreases rapidly according as the content of network molecules increases. Consequently, it is not the thickness of the cell that counts but the average distance between the network molecules. This explains the short decay times in comparison with the decay times (a few hundred milliseconds) in normal nematic cells. More particularly, decay times of less than one millisecond can be obtained.

The above-mentioned scattering properties of the gel can of course be used in many other optoelectronic devices, such as shutters.

The invention will be explained in more detail by means of the following example of the preparation of a liquid crystalline material according to the invention.

Example.

A display cell was composed of two opposite plates which are transparent to light and which are provided with an electrode of a material which is transparent to light and with rubbed polyimide layers. In the cell there was provided the liquid crystalline material consisting of the materials a) and b), for which purpose 5 % of diacrylate was used, represented on the formula sheet by formula 14 (known under the indication C6H), which diacrylate was added to 95 parts of a liquid crystalline material, marketed by BDH and known under the indication E7, consisting of a mixture of four substances, represented on the formula sheet by formulae 15-18. A photo-initiator in a quantity of 1 part by weight was added to said mixture, Irgacure 651 which is marketed by Ciba Geigy being used as the photo-initiator. The provision takes place by capillarity (under the influence of the surface tension). The orientation obtained corresponds with the direction in which the polyimide was rubbed. After said orientation, the liquid crystalline material was exposed to UV light (TLO9-Philips), so that a skeleton was formed on the basis of the acrylate which is represented by formula 14 on the formula sheet, which skeleton was present in the continuous phase of the material b) and it preserved the orientation independent of the fields applied and the influences to which the liquid crystalline material b) was subjected.

Claims

1. A liquid crystalline material in the form of an anisotropic gel consisting of a polymerized liquid crystalline material and a low-molecular liquid crystalline material, characterized in that the polymerized material a) forms a permenantly oriented network in the low-molecular liquid crystalline material b).

2. A liquid crystalline material as claimed in Claim 1, characterized in that material b) forms a continuous phase around the network of material a).

3. A liquid crystalline material as claimed in Claim 1, characterized in that material a) is selected from acrylates, epoxy compounds, vinyl ether compounds and thiolene compounds.

4. A liquid crystalline material as claimed in Claim 3, characterized in that the acrylate corresponds to formula 1, shown on the formula sheet, where A is a group denoting a bonding dash, -O- or - COO-, B is a mesogenic group examples of which are indicated by formulae 9-12, as shown on the formula sheet, and m and n are integers between 0 and 20.

5. A liquid crystalline material as claimed in Claim 3, characterized in that the epoxy compound corresponds to formula 3, shown on the formula sheet, where X corresponds to a group represented by formulae 4-8, shown on the formula sheet, B is a mesogenic group examples of which are indicated by formulae 9-12, shown on the formula sheet, and p is an integer having a value of 0-20.

6. A liquid crystalline material as claimed in Claim 3, characterized in that the material a) is a vinyl ether of formula 13, as shown on the formula sheet, and B and X have the same meaning as indicated in Claim 5.

7. A liquid crystalline material as claimed in Claims 1-6, characterized in that material a) is present in the gel in a quantity of 1-50 % by weight.

8. A liquid crystalline material as claimed in Claim 7, characterized in that the material a) is present in the gel in a quantity of 3-10 % by weight.

9. A liquid crystalline material as claimed in Claims 1-8, characterized in that substance b) is a non-polymerizable crystalline material.

10. A liquid crystalline material as claimed in Claims 1-8, characterized in that under the conditions of cross-linking substance a), substance b) is a non-polymerizable liquid crystalline material.

11. A liquid crystalline material as claimed in Claim 9, characterized in that substance b) is selected from the group of compounds represented by formulae 15-18 on the formula sheet, or a mixture thereof.

12. A liquid crystalline material as claimed in one of the preceding Claims, characterized in that the permanently oriented network is helically shaped.

13. A display cell comprising two opposite plates which are transparent to light as the substrate, which plates are provided with an electrode of a material which is transparent to light on the sides facing each other, said electrode carrying an orientation layer and a sealing material being provided between the ends of the plates, a liquid crystalline material being introduced in the space between the plates and the sealing material, characterized in that the liquid crystalline material is composed of at least two different liquid crystalline materials, as indicated in Claims 1-12.

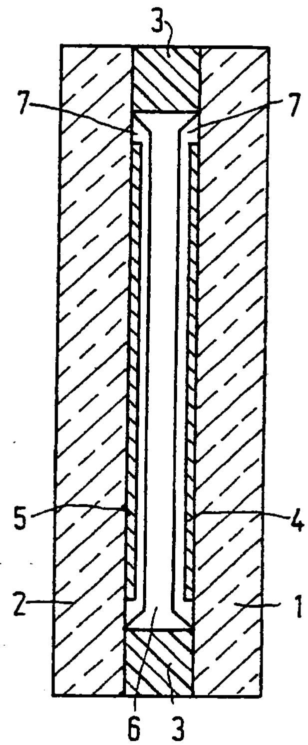

3
7
7
5
4
2
1
6
3

FIG. 1

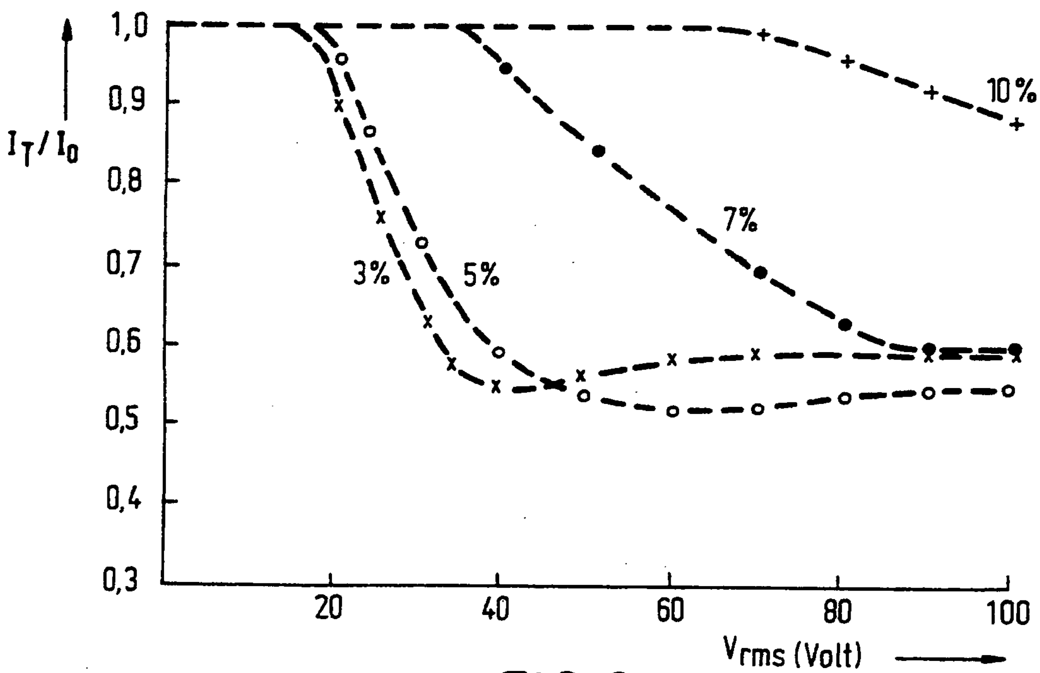

1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
I_T/I_0
10%
7%
3%
5%
20
40
60
80
100
Vrms (Volt)

FIG. 2

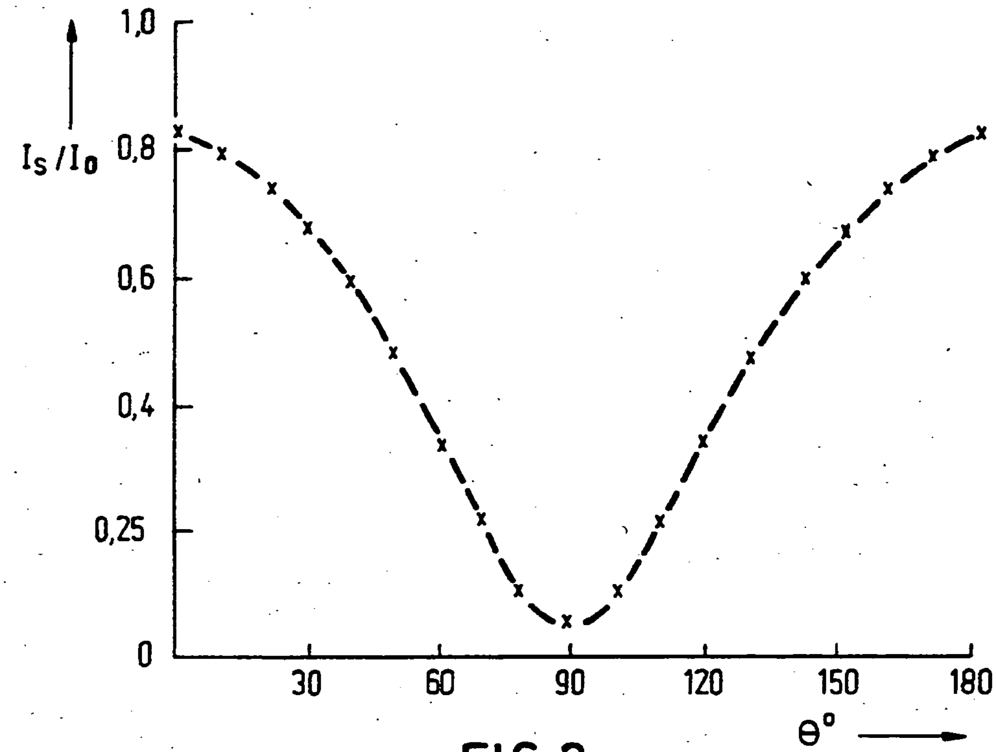

1,0
0,8
0,6
0,4
0,25
0
I_S/I_0
30
60
90
120
150
180
θ°

FIG. 3

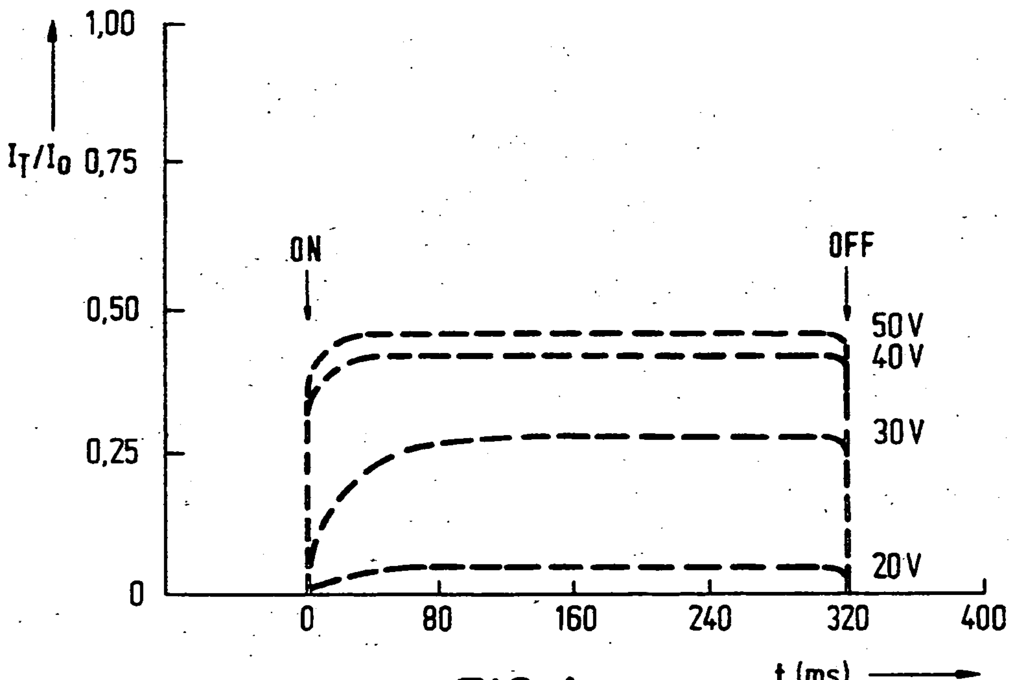
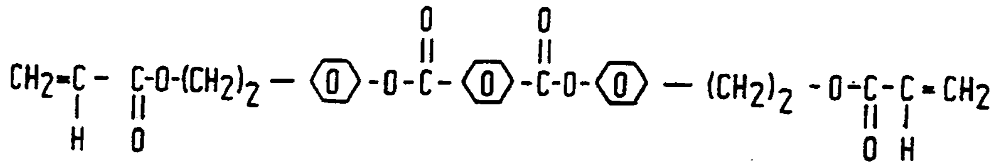
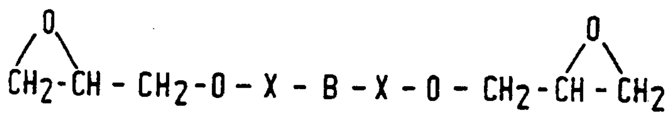

1,00
0,75
0,50
0,25
0
I_T/I_0
ON
OFF
50 V
40 V
30 V
20 V
0
80
160
240
320
400
t (ms)

FIG. 4

1. $CH_2=\underset{R}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}-O-\left[(CH_2)_m-A\right]-B-\left[A-(CH_2)_m\right]_n-O-\underset{O}{\underset{\|}{C}}-\underset{R}{\underset{|}{C}}=CH_2$

2. 

3. 

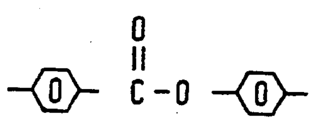
4. $-(CH_2)_p-$

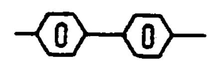
5. $-(CH_2)_p\ O-$

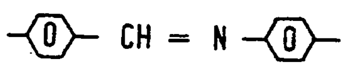
6. $-(CH_2-CH_2-O)_p-$

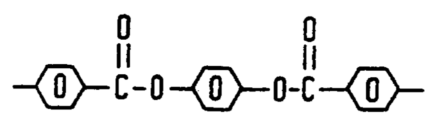
7. $-(CH_2)_p\ O-\overset{O}{\overset{\|}{C}}-$

8. $-(CH_2)_p\ \overset{O}{\overset{\|}{C}}-O-$

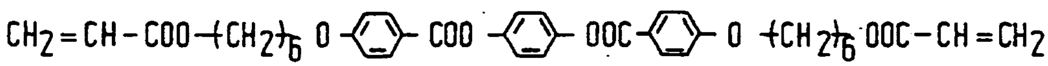
9. 

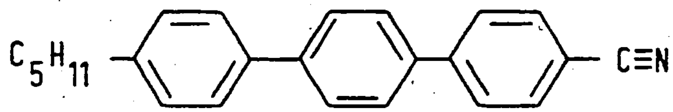
10. 

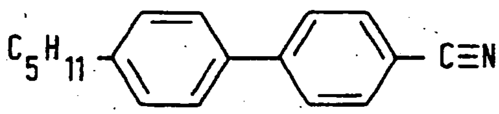
11. 

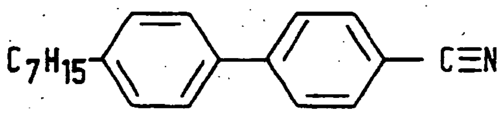
12. 

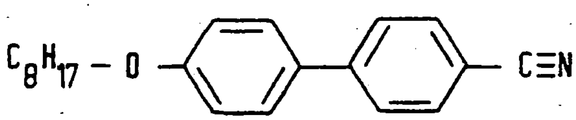
13. $CH_2=CH-O-X-B-X-O-CH=CH_2$

14. 

15. 

16. 

17. 

18. 

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EUROPEAN SEARCH REPORT

Application Number

EP 91 20 0773

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 842 380 (T. TAKAYANAGI) * Column 1, lines 3-12,25-68; column 3; column 4, lines 39-65; column 6, lines 20-30; column 7, lines 1-27 *	1-6,9-11, 13	C 09 K 19/38 G 02 F 1/1333
Y	EP-A-0 261 712 (PHILIPS) * Column 3, lines 1-55; column 5, lines 1-15, formules *	1-6,13	
Y	EP-A-0 292 244 (CANON) * Page 3, lines 13-31; page 10, lines 19-21; page 11, no. 19; page 12; page 20, lines 1-11,18-26; page 21, lines 10-16; page 31, lines 6-13; figure 1 *	1-6,13	
A		7,8,12	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 09 K 19

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	05 July 91	BOULON A.F.J.

CATEGORY OF CITED DOCUMENTS

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